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THEORY OF POLARIZATION OF IONIC CRYSTALS

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The present work shows that 1) for alkali halide crystals the classical theory of polarization of ionic crystals, based on the works of Lorentz and Born, is insufficient; 2) the concept of overlapping of electron shells in ionic crystals which was put forward by Pauling and Mott is subjected to criticism; 3) a scheme for the polarization of ionic crystals which takes into account the deformation of electron shells can be developed; and 4) the theoretical representations developed agree closely with experimental data.

## Introduction

Typical representatives of ionic crystals are alkali halide crystals, which occupy a special position in the theory of solids. The simplicity of their highly symmetrical cubic lattice and the elementary character of their electrostatic ionic bond have made them a favorite subject of theoretical works, whose authors have linked together directly or indirectly three basic characteristics of the ionic crystal; namely, the dielectric permittivity  $\epsilon_{\infty}$ , resonance frequency of polarized ionic oscillations  $\omega_0$ , and the corresponding wave vector  $\lambda_0$ .

Born calculates a crystal's natural frequency using the formula

$$\omega_0^2 = \frac{q^2}{\epsilon_{\infty} \epsilon_0} \left( \frac{1}{m_c} + \frac{1}{m_a} \right), \quad (1)$$

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where  $q$  is the ion charge;  $v$  the volume associated with the stoichiometric molecule;  $\epsilon_0$  the square of the "optical" index of refraction extrapolated to zero frequency;  $m_c$  and  $m_a$  the masses of cation and anion. In deriving his formula Born represented a diversity of polarized fields by a static field and rapid oscillations. At frequencies close to and higher than the natural frequencies of polarized lattice oscillations the field polarizing the electrons is, according to Born,

$$(E_p)_e = E(1 - \frac{4\pi}{3}\beta_e)^{-1}$$

where  $\beta_e$  is electron polarizability per unit volume; for the distortion of an ion as a whole he assumes

$$(E_p)_i = E,$$

i.e., equal to the average macroscopic field. At the same time for a static field and low-frequency oscillations Born keeps the Clausius-Mosotti formula (true, Born avoids using it; he practically refutes the comparison between dielectric permeability and bulk modulus).

In spite of the almost universal inaccuracy of Born's polarizing field theory, the calculation by formula (1) of the difference  $\epsilon_\infty - \epsilon_0$  from experimental values of  $\lambda_0'$  (minimum for the passage of "light") gives fair agreement with experiment for some halides (LiF, NaF, NaCl, KCl, KBr, KI); but results are worse in the case of NaBr, RbCl, RbBr, RbI, where the "nonbond coefficient" lies in the interval 1.34-1.68. Besides, it is inadmissible in principle to substitute experimental data for formal proof in evaluating a theory, when the chance for compensation of systematic errors or discounted effects of signs is great.

Frankel [2] derived the formula linking dielectric permeability with bulk modulus (by means of the constant  $n$ —the exponent in the expression for the energy) in the form

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3}\beta_i = \frac{4\pi}{k\gamma(n-1)}, \quad (2)$$

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where  $\beta_i$  is the ionic polarizability per unit volume;  $k$  is Madelung's constant; and  $\gamma$  is the geometric structural coefficient (NaCl type:  $k=1.744$  and  $\gamma=2$ ; CsCl:  $k=1.76$  and  $\gamma=1.54$ ).

For most alkali halide crystals the left part of expression (2) is 1.5-2 times less than the right part; for example, for NaCl ( $\epsilon_\infty=5.77$ ,  $\epsilon_0=2.328$ ,  $n=7.9$ ) the left part yields the number 0.31 and the right yields 0.52 (Note: In the calculations, here and below,  $\epsilon_0$  is according to Erner's most reliable data; for  $\epsilon_0$  see [3] and for  $n$  see [1], first column in the table on p 271).

Skaniavi [4] calculated in different ways the dielectric permeability of alkali halide crystals, proceeding from various expressions for lattice energy and polarizability of ions in solutions and using the formulae of Lorentz and Mott for the polarizing field (10 variants in all).

First of all, it should be noted that the use of the number dissolved ions in calculations of polarizability of a crystal is inexpedient and calls forth considerable doubt. It is known (see, for example, [1], p 298) that ion polarizability depends upon the ion's environment. Further, the use of Slater's values for  $n$ , calculated from the relations between compressibility and pressure, is baseless; for this is equivalent to a "further extrapolation" of the approximate function of repulsion energy; still less usable are Hildebrand's numbers for  $n$  and Born's for  $\rho$ . Their use would be relevant only if the results of calculation were compared with the values of dielectric permeability for  $T \cong 0$ .

The most natural method of calculation, with a direct comparison of the quantities  $\epsilon_\infty$ ,  $\epsilon_0$ , and  $E_v$  by the method of formula (2), was not carried out in the works discussed.

Only the application of Mott's quite arbitrary formula for polarized fields permitted the calculated and experimental values of  $\epsilon_\infty$  to be

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brought into formal agreement. (Note: We cannot consider as satisfactory Skavani's point of view, in which the discrepancy between calculated and experimental values of  $\epsilon_{\infty}$  for K, Rb, Cs halides is founded to be 1.3-2 times that as calculated by Clausius-Mosotti.)

The foregoing deficiencies of other works permit the author to hope that his present work, characterized by its refutation of the "point scheme" of ionic polarization of crystals, will not be considered superfluous.

#### 1. On the Deformation of Electron Shells

Wave mechanics represents a single atom (ion) as a nucleus surrounded by an "electron cloud", whose average charge density over a period of time differs from zero during any discharge from the nucleus.

Two basic points of view can be formulated: a) at the approach of chemically inert (zero valent) atoms or ions, their electron shells overlap (Pauling [5], p 328; Mott and Gurney [6]) and b) the electron shells repel each other and are deformed but do not overlap; in the transitional zone a sharp minimum of charge density is observed.

Figure 1 demonstrates these two concepts: it is assumed here that the cation experiences practically zero deformation in comparison with the anion.

Figure 2 pictures the distribution of electron density in a NaCl crystal which is constructed on the basis of x-ray data (see Syrkin and Dyatkin [7], p 375). A close study of this <sup>picture</sup> ~~figure~~ refutes the first point of view to the advantage of the second; to begin with, there actually exist in the contact zone regions "zero" (i.e., relatively extremely small) charge density; further, but not less important, in the Cl-anion. The surface corresponding to the density  $\rho_{0.5} = 0.5 \frac{\text{electrons}}{\text{\AA}^3}$  clearly has "buckling", which are due to the action of electron shells of the neighboring cations. For

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the surface  $\rho_{1.0}$ , more remote from the cation, this buckling is also noticeable, though naturally expressed less sharply.

It would certainly be incorrect to represent the electron shells of neighboring ions as absolutely isolated, since there must exist between them some kind of transitional zone. According to Frenkel' [8], it can be treated as a zone of "collectivized electrons"; here however, we are talking in contrast to metals, about "ineffective" collectivization characterized by small electron density in the transitional zone and monotonic increase of the repulsive force with approach of ions.

Thus even with the adoption of the concept of collectivization, a scheme of independent electron shells, acting one on another like elastic bodies, can be employed in the first approximation.

Let us consider the picture of the phenomena which occur when an ionic crystal is polarized; let us superimpose this picture on elementary polyhedra with centers coinciding with the anion nuclei and assume to begin with that the cations are absolutely rigid.

As an example let us take the concrete case of coordination number 6 (a crystal of the type NaCl, in which the elementary polyhedron is represented as a regular octahedron);

Let the field be directed along the main axis of the crystal lattice. Let us take the anion nucleus as the immobile origin. The displacement by a distance  $\xi$  of the rigid cations of the sectors  $(Me\frac{1}{6})_6^+$  (Figure 3) immediately creates an electrical moment

$$\mu_{0i} = q \xi$$

simultaneously the left cation displaces to the right the electron shell of the anion and <sup>the</sup> right cation in being repelled from the anion center to a certain degree makes possible the "straightening" of the corresponding segment of the anion's electron shell, and this segment also is displaced to the right in the direction of the field.

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The displacement of the anion's electron shells in the direction of the field creates a moment opposite to the main moment  $\mu_{oi}$ . Thus the resulting moment of the elementary polyhedron, when an ionic crystal with rigid cations is polarized, is

$$\mu = \mu_e + q\xi - \mu_a \quad (4)$$

where  $\mu_e$  is the moment due to the immediate polarization of the electron shells by the electric field.

It can be shown in the case of large cations that their deformation cannot be disregarded; therefore, considering the direction of displacement of the cation's shells when they are being distorted, we are satisfied that the directions of the moments  $\mu_c$  and  $\mu_{oi}$  coincide hence and the resulting moment is

$$\mu = \mu_e + q\xi - \mu_a + \mu_c \quad (5)$$

Multiplying both sides of (5) by  $N_1$  - namely the number of elementary polyhedra per unit volume  $\frac{m}{\lambda}$  - and setting  $E_p = 1$ , we obtain from (5).

$$\beta = \beta_e + \beta_i = \beta_e + \beta_{oi}(1 - \zeta), \quad (6)$$

where  $\beta$  is total polarizability per unit volume; the quantity characterizes the influence of the supplementary moments which are due to the deformation of the electron shells; in the absence of deformation or when  $\mu_c = \mu_a$ , we have  $\zeta = 0$ . We can also write

$$\zeta = \zeta_a - \zeta_c \quad (7)$$

where

$$\zeta_a = \frac{\mu_a N_1}{\beta_{oi} E_p} \quad \text{and} \quad \zeta_c = \frac{\mu_c N_1}{\beta_{oi} E_p}$$

Already the establishment of relations (6) and (7) makes it possible to make certain predictions. It is natural to consider that large anions are deformed more strongly than small ones; thus for halides with the same rigid cation ( $\text{Li}^+$ ,  $\text{Na}^+$ ), the quantity  $\zeta$  must increase as one moves in the series from  $\text{Li}(\text{Na})\text{F}$  to  $\text{Li}(\text{Na})\text{I}$ .

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Particularly small values of  $\zeta$  must correspond to combinations of small anion  $F^-$  with large cations  $K^+$ ,  $Rb^+$ ,  $Cs^+$  in consequence of total or substantial partial compensation of the moments  $\mu_a$  and  $\mu_c$ .

## 2. Calculation of the "Counter-Moment" for Alkali Halide Crystals

The coefficient of quasi-elastic force  $f$  corresponding to polarization of the elementary polyhedron can be calculated from the bulk modulus  $E_v$  if one knows parameter  $S_1$ , which indicates the influence of repulsion of similar charges under all-sided compression. We have (see [3])

$$f = \frac{3\gamma r_0 E_v}{1 + S_1}. \quad (8)$$

In the "point scheme" of polarization, which does not consider ion deformation, the polarizability of the elementary polyhedron is

$$\alpha_{oi} = \frac{q^2}{f}; \quad (9)$$

consequently,

$$\beta_{oi} = \frac{q^2 N d (1 + S_1)}{3\gamma r_0 E_v (M_c + M_a)}, \quad (10)$$

where  $d$  is crystal density;  $N$  is Avogadro's number;  $M_c$  and  $M_a$  are atomic weights of cation and anion. From (6) it follows that

$$\zeta = \zeta_a - \zeta_c = 1 - \frac{\beta_i}{\beta_{oi}}. \quad (11)$$

In calculating the ionic polarizability  $\beta_i$  we used the well known relation from Lorentz' theory of polarizing fields.

$$\beta_i = \frac{3}{4\pi} \left( \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} - \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \right). \quad (12)$$

The original data and the results of calculations are presented in Table 1.

## 3. Consideration of the Results Obtained

Figure 4 gives the relation between  $\beta_{oi}$  ("polarizability by geometric displacement") and the anion radius  $[R_a]$ .

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In the lithium halide series  $\beta_{0i}$  increases noticeably with increasing anion radius; this effect<sup>is</sup> due to the decrease of interaction forces and the increase of distance between  $\text{Li}^+$  and large halide ions as a result of anion repulsion (for  $\text{LiF}$  we have  $S_1 = 0.15$ ; for  $\text{LiI}$ , 0.64).

In the case of sodium and potassium halides  $\beta_{0i}$  practically does not depend on anion discussions, while for rubidium halides a weak dependence ( $\sim 10\%$ ) is observed (Note: The point corresponding to  $\text{RbBr}$  clearly lies outside the curve; later calculations take the "compensated" quantity  $\beta_{0i} = 0.11$ ,  $\zeta = 0.47$ ).

Let us pass to the quantity  $\zeta$ . As is evident from Figure 1, the minimum value of  $\zeta$  corresponds to the weakly polarized ion  $\text{F}^-$ ; the maximum corresponds to the large iodine ion  $\text{I}^-$  (see the table of polarizability Table 2). In the fluoride series  $\zeta$  falls 4 times in the transition from  $\text{NaF}$  to  $\text{RbF}$ , which is completely and naturally explained by the compensation of momenta  $\mu_a$  and  $\mu_c$  for the interaction of small anion with large cation.

In graphically representing parameter  $\zeta$  characterizing the deviation of polarizability from the classical point scheme, we employ the polarizability of anion  $\alpha_a$  as the independent variable (Note: Here and later we are guided by the simple idea of a relation between ion deformability and polarizability; however, we should not expect ions of sharply varying types, though possessing equal polarizability, necessarily to have equal capacity for deformation; quantitative correspondence probably exists for similar ions; for example in the anion series  $\text{F}^-$  to  $\text{I}^-$  or the cation series  $\text{Li}^+$  to  $\text{Rb}^+$ ).

Figures 5 and 6 show the curves  $\zeta = f(\alpha_a)$  for halides of  $\text{Li}$  and  $\text{Na}$ ,  $\text{K}$  and  $\text{Rb}$ ; they appear as smooth convex curves monotonically rising with increase of  $\alpha_a$ .

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It is natural to ask how, for high  $\alpha_a$ 's (large anions),  $\text{Li}^+$  creates in anions larger "deformation moment" than does  $\text{Na}^+$ . From the point of view of primitive geometrical representation it would seem that moving cations of larger size must create also greater deformation.

For an explanation of the nature of the thing let us turn our attention to the nonequality of condition in the case of small and large ions; actually the charge density in the contact zone is directly dependent on the magnitude of forces compressing the ions, i.e. coulomb forces; therefore under any equal conditions the greater the moment  $\mu_a$  or the quantity  $\zeta_a$ , the greater the coulomb force  $\frac{q^2}{r_0^2}$ , where  $r_0$  is the distance between centers of neighboring unlike ions.

As a rough approximation we can attempt to study this effect, by making the moments  $\mu_c$  and  $\mu_a$  (or, correspondingly,  $\zeta_c$  and  $\zeta_a$ ) proportional to the coulomb force; then, reducing the quantity  $\zeta$  to the standard coulomb force which characterizes, according to our selection, the LiF crystal, we have

$$\zeta' = \zeta \frac{r_0^2}{[\epsilon(\text{LiF})]^2} \quad (13)$$

Figure 7 shows that in the absence of moment  $\mu_c$  or the presence of only an insignificant quantity ( $\text{Li}^+$  and  $\text{Na}^+$  being extremely weakly polarized). The "reduced" quantity  $\zeta' \cong \zeta_a'$  is a linear function of polarizability  $\alpha_a$ . Here, as might be expected, the larger cation  $\text{Na}^+$  creates a greater effect, than  $\text{Li}^+$ .

Let us now consider in somewhat greater detail how cation deformation influences the quantity  $\zeta$ . Since according to (5) the value is

$$\zeta = \frac{\mu_a - \mu_c}{q \xi}, \quad (14)$$

i.e., relative to unit displacement, then it is necessary in comparing the cases  $\mu_c = 0$  and  $\mu_c \neq 0$  to make the displacement  $\xi$  the same in both cases.

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The displacement  $\xi$  is composed of the deformations of anion and cation; thus,

$$\xi_a = \xi - \xi_c; \quad (15)$$

consequently  $\xi_a$  also will be less than when  $\xi_c = 0$ . The quantity  $\xi = \xi_a - \xi_c$  decreases on account of the appearance or increase of the term  $\xi_c$  and as a result of the decrease of  $\xi_a$  and  $\xi_c$ .

In the transition to larger anions with greater polarizability, the fraction of cation deformation  $\xi_c$  and the component  $\xi_c$  related to it drops sharply; as a result a convex curve instead of the linear relation is obtained as the characteristic for K and Rb halides (Figure 8).

In passing, we note that when  $\xi = f(\alpha_a)$  the curves form a normal succession: larger cations create larger moments in the anion.

In conclusion I thank Prof. Ya. I. Frenkel' for his assistance in this work.

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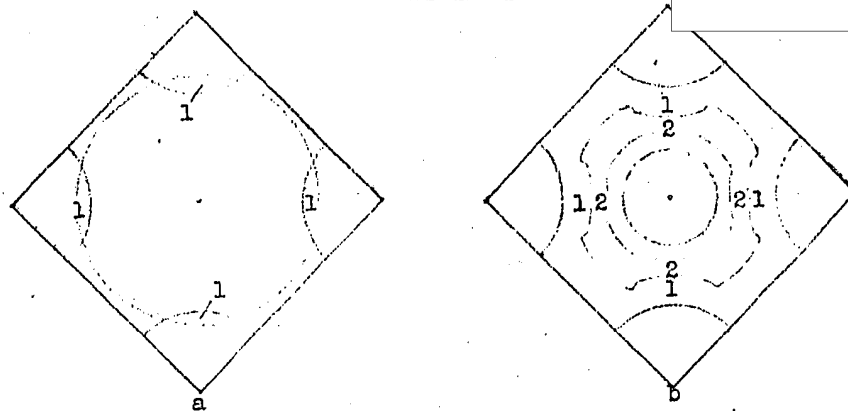


Fig. 1. Schemes of interaction of "closed" electron shells.  
a - scheme of Mott-Pauling; b - schematized real picture of interaction.  
1, 2 - zones of intensive deformation.

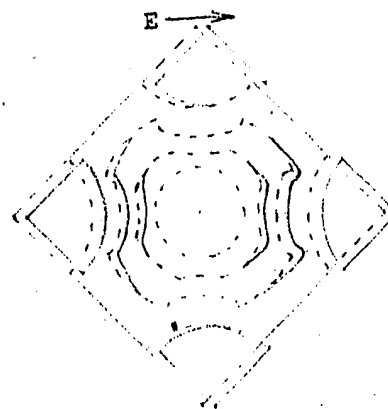


Fig. 3. Scheme of polarization of ionic crystal

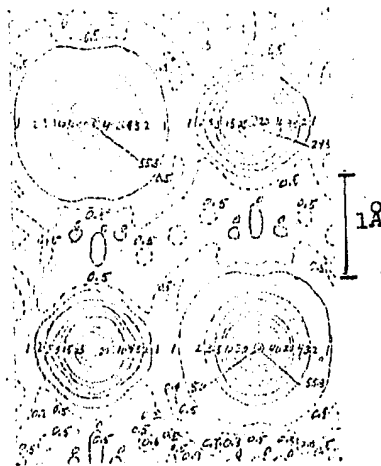


Fig. 2. Distribution of electron density in a crystal of NaCl (according to Syrkin and Dyatkina).

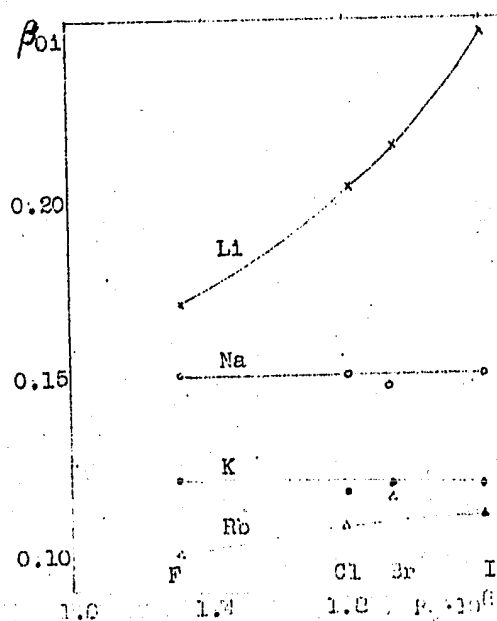


Fig. 4

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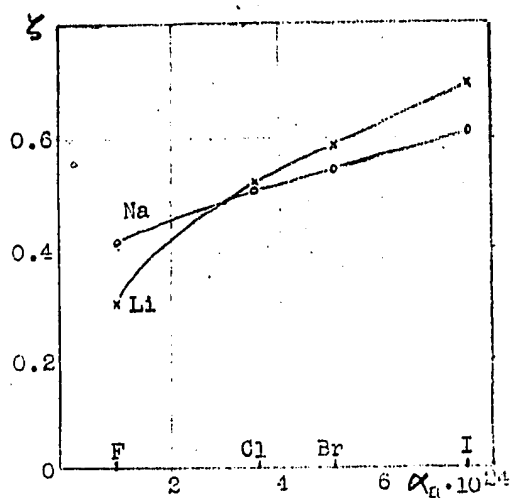


Fig. 5.

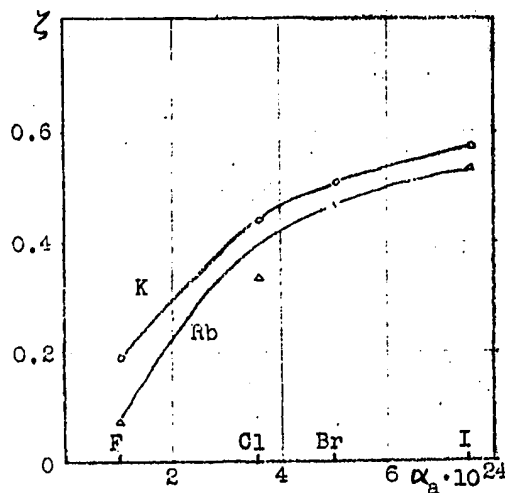


Fig. 6.

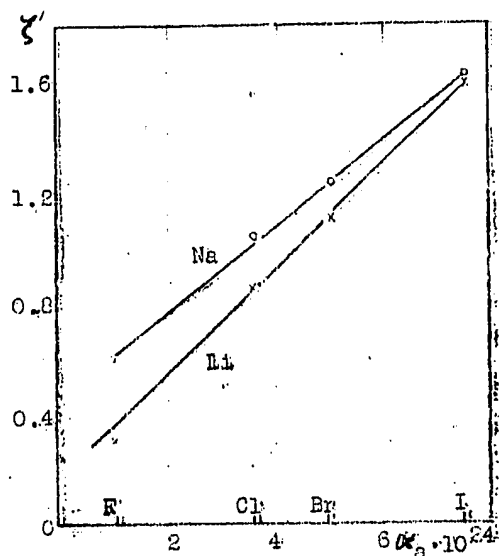


Fig. 7.

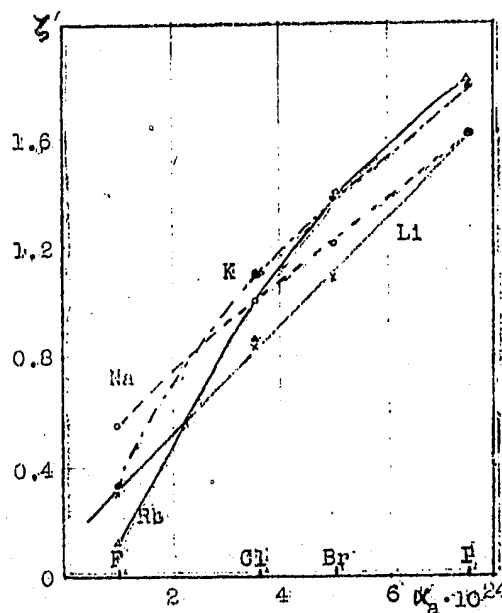


Fig. 8.

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Table 1

Mat- ter	$\epsilon_{\infty}$	$\epsilon_0$	$E_{\text{ion}}$ eV dynes/ cm	$r_0 \cdot 10^8$ cm	$M_c - M_a$	$1 - a_1$	$d$	$\beta_1$	$\beta_{01}$	$\gamma$
LiF..	9.2	1.885	6.80	2.01	25.94	1.15	2.295	0.1202	0.172	0.500
LiCl.	11.05	2.36	2.89	2.57	42.40	1.34	2.068	0.0977	0.205	0.520
LiBr.	12.1	3.97	2.20	2.74	86.82	1.42	3.464	0.0905	0.217	0.584
LiI.	11.3	3.34	1.56	3.03	133.86	1.64	4.061	0.0733	0.245	0.71
NaF.	4.9	1.780	4.73	2.31	42.00	1.07	2.79	0.0853	0.150	0.411
NaCl.	5.77	2.330	2.34	2.81	55.46	1.16	2.163	0.0733	0.150	0.511
NaBr.	5.99	2.60	1.96	2.87	102.32	1.19	3.205	0.0660	0.147	0.550
NaI..	6.60	3.05	1.44	3.23	149.43	1.23	3.637	0.0580	0.150	0.613
KF...	6.05	1.605	3.12	2.85	58.10	1.02	2.48	0.0976	0.121	0.193
KCl..	4.76	2.133	1.72	3.14	71.33	1.07	1.928	0.0637	0.112	0.223
KBr..	4.78	2.539	1.43	3.29	119.37	1.09	2.75	0.0587	0.119	0.303
KI...	4.94	2.616	1.17	3.56	133.02	1.13	3.123	0.0510	0.119	0.571
RbF..	5.91	1.94	3.0	2.61	104.45	1.05	3.62	0.0915	0.100	0.075
RbCl.	5.20	2.164	1.5	3.27	110.91	1.06	2.76	0.0719	0.106	0.334
RbBr.	4.70	2.538	1.26	3.40	165.57	1.07	3.35	0.0577	0.116	0.502
RbI..	4.81	2.574	1.05	3.60	212.37	1.10	3.55	0.0513	0.111	0.538

Table 2

	$\alpha_c \cdot 10^{24}$		$\alpha_a \cdot 10^{24}$
Li <sup>+</sup>	0.03	F <sup>-</sup>	0.96
Na <sup>+</sup>	0.19	Cl <sup>-</sup>	3.6
K <sup>+</sup>	0.89	Br <sup>-</sup>	5.0
Rb <sup>+</sup>	1.5	I <sup>-</sup>	7.6
Cs <sup>+</sup>	2.6		

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